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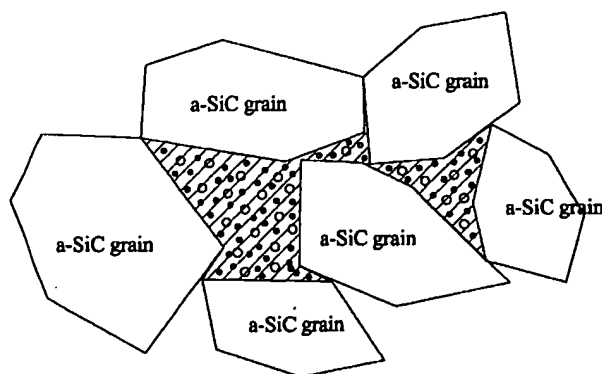
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(54) Title: **POROUS CERAMIC STRUCTURES AND A PREPARING METHOD**



Green body grain structure  
Manufacturing temperature range 10-80°C  
Alpha SiC (a-SiC grains)  
• - Carbon black or graphite  
○ - Si or SiO<sub>2</sub>  
⊙ - Organic binders

(57) Abstract: A method for preparing a ceramic porous structure comprising a mix of: alpha silicon carbide primary particles having a size ranging between 1 and 475 µm, a silicon source other than an SiC compound, organic particles having a size of 0.00001-20 µm, at least one organic binder forming a paste or fluid from said mix and selected suitable liquid(s), forming the paste into a green body and drying it at low temperatures to form a solid non-porous body, subjecting said body to pyrolyzing conditions in a furnace under a protective atmosphere to convert the organic binder to a medium temperature carbon binder, melting the silicon source and reacting it with the carbon binder or particles at high temperature thus creating nano-fine beta-SiC, which is further converted to nano-fine alpha-SiC and at very high temperature sublimated to a gas followed by condensing said gas at the primary particles grain boundaries so as to bond the primary particles together to form a rigid porous structure. The silicon source may be silicon metal having a particle size of 0.01-30 µm, silica having a particle size of 0.001-20 µm, a silicone or silane in liquid stage.

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

Porous ceramic structures and a preparing method.

### Field of the invention

The present invention relates in general to porous silicon carbide structures,  
5 which may serve several purposes in the environmental area as well as the  
area of general technical ceramics.

Separation of particles from a fluid, i.e. a liquid or a gas, is usually performed by  
passing the fluid through a wall of porous material, the particles being  
10 accumulated on the one side of the porous wall. The accumulated particles are  
subsequently removed by oxidation, back flossing, etc. The porous material  
may be of a ceramic composition in order to withstand the demand to  
temperature and corrosive stability.

15 To eliminate the possibility of particles passing through the filter wall, a  
membrane may be applied to the filter wall(s). Hereby the porous material may  
act as a membrane carrier or support.

The pore size of the filter material, i.e. the membrane carrier or support, may be  
20 chosen so large that the filter causes no or only little pressure drop in the fluid  
passing the filter wall, either transverse or longitudinal relative thereto.

Conventionally, a membrane having a pore size smaller than that of the filter  
body material has been deposited on the membrane carrier for increasing the  
25 filtering efficiency of the filter. Typically, such membrane is required when  
filtering very small particles or suspended matter. The membrane prevents  
penetration of the particles into the matrix of the filter body material, which is  
advantageous as the particles are not readily removed from the interior of a  
filter body having larger pores.

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Another aspect of the invention concerns bodies used as transformers of short  
wave energy radiation from the sun into long wave energy. Radiation from the

sun may be reflected by constantly adjustable mirrors, which by the adjustment concentrate the radiation onto high temperature stable bodies, which are thus heated. The heated bodies are cooled by a heat-collecting medium such as a molten salt, sodium metal, a gas or atmospheric air. The heat-collecting medium thus heated transfers the energy to a steam generator for the production of steam which subsequently is lead through a steam turbine. The heat-collecting medium, which is cooled hereby, may be re-circulated in order to maximise system efficiency. The surface, which is heated by the reflected sun, must be cooled all the time in order to avoid material melting or evaporation.

### Background of the invention

SiC is more corrosion resistant at high temperatures than most other ceramics and metals. At temperatures up to 850°C, the service life of SiC filter bodies will probably not depend on corrosion. However, at higher temperatures, gasses containing large amounts of water vapour/alkali/chlorine/sulphur will corrode the protecting SiO<sub>2</sub> layer on the SiC particles in the filter body and oxidation of the SiC particles may be accelerated. Oxidation tests have shown no weight change of SiC material exposed to 900°C for 2000 hours in an oxidising atmosphere. SiC also shows good corrosion resistance to liquids such as sodium hydroxide solutions currently used for liquid cleaning of filters being used in the food industry.

The base material for powder technology filter bodies is preferably ceramic particles, which in average usually have a mean particle size in the range of 10-500 µm, such as in the range of 15-350 µm, preferably in the range of 30-200 µm, giving filters with pore sizes ranging from 3-55 µm.

When SiC is to be used, commercial grades of SiC are presently the preferred starting products for producing the porous silicon carbide structures, such as Mesh 40, 60, 80, 120, 150, 180, 220, 280, 320, 360, 400, 600, 800, 1000, 1200 (according to FEPA standards).

Production methods normally employ continuous barrel/auger extrusion, but other commonly known ceramic shaping processes, such as tape-casting, iso-static casting, slip-casting and other casting methods may also be used.

- 5 Presently, the preferred manufacturing method of filter bodies is extrusion and sintering of a paste comprising particles of silicon carbide material, a permanent binder system, one or more green binders and one or more liquids.

10 Thus, when using SiC in a filter body, a permanent binder is mandatory and needs to be incorporated in the paste to be shaped and sintered to form the porous filter structure. During sintering, this permanent binder will interconnect the primary SiC particles and solidify the filter body in the desired shape in a manner so that the SiC particles, as described above, directly define the pores of the material.

15 During high temperature firing it is preferred that the primary grain do not change size. Extra control of the re-crystallisation may be effected by adding some ultra fine carbon powder into the green mix. The rate of re-crystallisation can be controlled or reduced by adding 0,1-10% preferably 2-5% of carbon powder.  
20

Extrusion of a material based on a sub-micron or micro-crystalline powder to produce a honeycomb monolith or tubes using a pore forming agent to form the porosity of the filter body is an alternative method for producing structures with  
25 a controlled pore size. The pore forming agent will preferably be organic particles of a controlled size in the range of 5-1000  $\mu\text{m}$ , preferably in the range of 10-100  $\mu\text{m}$ . The pore forming agent may be manufactured from various materials, such as combustible or organic materials such as sawdust, granulated polyurethane powder, a polymer, or carbon powder. When the  
30 shaped green body is oxidised, after drying, at high temperatures in an oxidising atmosphere, the pore forming agent will evaporate or pyrolyze and, thus, leave pores of a controlled size.

As filter bodies may be manufactured having a well-defined pore size, the pore size can be chosen depending on the desired filtering efficiency of the filter body. Thus, depending on requirements for the maximum system weight, the powder based filter body may be manufactured with relatively thin walls. Especially due to the high mechanical strength of the preferred filter body consisting almost entirely of SiC, thin filtering walls may be produced. Wall thickness may be 0.1-10 mm, preferably 0.8-2 mm. The cell pitch, which is the combined measured figure in millimetres of the wall thickness and the channel width, may be in the range of 1-25 mm, preferably 2-10 mm.

Silicon carbide, SiC, exists as alpha and beta crystal phases. An SiC body fired at temperatures above 2000°C will constitute of pure alpha SiC only. The beta type is preferred in a binder system, but is very expensive and not commercially available. Therefore, the alpha type is generally used as raw binder material available commercial within the FEPA classification, i.e. Federation of the European Producers of Abrasives. FEPA type of SiC is available in grain sizes ranging in fractions from F-1200 being 7.6 micrometers (7.6  $\mu\text{m}$ ) in mean grain diameter to F-4 being 4.8 millimetres (4.8 mm) at relatively low cost. For lower sizes than F-1200 or 7.6  $\mu\text{m}$  the measure is expressed as surface area per gram powder,  $\text{g/m}^2\text{:BET}$ . FCP-15 is the finest commercial available powder available from Norton or Saint-Gobain manufactured by a combination of grinding, milling and crushing processes. Also available as FCP-7 and FCP-13, but not finer than FCP15 with particle size around 0.6  $\mu\text{m}$ . Other vendors like Superior Graphite Inc. and H.C.Starck GmbH offer similar products with 15-19  $\text{g/m}^2\text{:BET}$ , all regarded as sub-micron powders with particle size larger than 0.5  $\mu\text{m}$ .

#### Prior art

Ceramic Industry/107, January 1989 contains an article concerning silicon carbide fibers, wherein it is explained that commercial SiC is produced in an electric furnace from a mixture of coke and silica sand (> 99, 4%  $\text{SiO}_2$ ) which

sometimes also contain sawdust and salt or another binder. An electric current passed between permanent electrodes located at both ends of the furnace, and through a graphite core produces a temperature higher than 2200°C, at which point crystals of silicon carbide form from the sand-coke charge. Beta-SiC (cubic) forms at 1400-1800°C and alpha-SiC (hexagonal) forms at temperatures > 1800°C. If used, the sawdust burns out keeping the mass porous and the salt assists in the removal of impurities through a formation of volatile chlorides. A furnace run takes 36 hr. Another method used to form SiC pieces is by vapor deposition of silicon unto a heated graphite or carbon surface.

Silicon carbide is manufactured in many complex bonded shapes such as silicon carbide refractories, which are classified on the basis of the bonds used. Associated type bonds are oxide or silica, clay, silicon oxy-nitride and silicon nitride as well as self-bonded. The dens material contain 85-99% SiC; the clay-bonded contain 75-80% SiC; and the semi silicon carbide are still lower in SiC-content.

Silicon carbide fibers are continues polycrystalline materials that are used for reinforcement of ceramics, metals and polymeric materials. The fibers generally contain a bonding agent such as silicon, which frequently limits the utilization temperature to 1300-1400°C. Some manufacturing technique utilizes a core of some other material such as graphite fibers onto which silicon carbide is coated by chemical vapor deposition. Diameters are typically ranging from 20-150 µm.

However, this article does not disclose nor suggest any method of producing a porous structure comprising a mixture of relatively coarse alpha-SiC primary particles bonded together by gas phase deposited SiC produced *in situ* from a silicon source and a carbon source.

WO 94/22556 discloses the manufacture of a filter body made of SiC particles prepared from a paste consisting of 60 – 70 wt% coarse SiC particles (10-250 µm diameter), 5 – 15 wt% fine SiC (sub-micron) particles, 3 - 10 cellulose ether

(organic binder), and necessary solvents, lubricants and/or plastifiers (Example 1, pages 19-23, and Example 2, pages 24-26). Additionally, the material to form the basis of the preferred SiC-based materials typically comprises a smaller amount (up to 15 %wt of the total weight) of a fine-grain (typically in the order of 0.3-2  $\mu\text{m}$ ) sintering additive such as SiC and/or  $\text{SiO}_2$  and/or carbon black. - The paste is extruded, and the extruded bodies are dried, e.g. in a microwave oven, whereupon the temperature is elevated to a temperature in the order of 200-600°C to evaporate (pyrolize) the binder, after which pyrolysis the bodies are sintered in e.g. an electrical heated furnace in an argon atmosphere for 15 to 240 minutes at temperatures above 2200°C, such as 2300°C (page 23, lines 25 – 30). – However, this publication does not contain any indication that the fine (sub-micron) SiC particles can be omitted from the recipe as permanent sintering additive.

Examples 6 of WO 94/21900 and EP 0 689 639 B1 describe the manufacture of filter segments made of SiC. A plastic mixture is manufactured by mixing 70 wt% Mesh 240 Sika I SiC particles with 10 wt% SiC having a particle size of about 1  $\mu\text{m}$ . Plasticity is obtained by adding to the mixture 6 wt% methylcellulose, 18 wt% water and 6 wt% ethanol. The paste prepared from these ingredients is extruded to green bodies, which are dried for 10 to 200 hours under controlled humidity and temperature (room temperature to 100°C) (EP 0 689 639, column 16, lines 39 – 43). Sintering is carried out in a furnace at temperatures up to 2450°C. The binder is removed due to pyrolysis when heated to a temperature in the range of 300-500°C. The atmosphere in the furnace is typical argon buffered by the gaseous species Si/SiO/CO. The sintering of the coarse-particle SiC in the filter segments is enhanced by the presence of the ultra-fine grained SiC either added directly in the paste, or generated from a reaction between the optionally added  $\text{SiO}_2$  and/or carbon black (or pyrolyzed binder) also added to the paste (column 17, lines 4 – 14). Due to the smaller radii of curvature, the fine-grain SiC particle fraction evaporates before the larger SiC particles constituting the actual filter segment. Subsequently the evaporated fine-grain particle fraction condenses in the



particle contacts between the larger particles giving a full SiC inter-grown porous structure. Thus, as the sintered material is now constituted by the larger SiC particles interconnected by the SiC formed by the evaporated and subsequently condensed fine-grain SiC particles, the initial size and the size distribution of the large SiC particles directly defines the pore size and the porosity of the sintered material. The porosity of the sintered material is in the order of 50% and the pore size is in the order of 35  $\mu\text{m}$  (column 17, lines 15 – 28). This structure is said to have a high physical strength and thermal and electrical conductivity as the filter segment consists substantially of only one material, SiC, and no other materials having less optimal properties are present in the sintered structure (column 17, lines 29-33). As the amount of SiC condensed at the particle boundaries may be controlled by the amount of added fine-grain SiC, strong interconnections in the particle boundaries may be obtained (column 17, lines 29 – 32).

Thus, these publications mention that the sintering of the coarse-particle SiC in the filter segments can be enhanced by the presence of the ultra-fine grained SiC either added directly in the paste, or generated from a reaction between optionally added  $\text{SiO}_2$  and/or carbon black (or pyrolyzed binder) also added to the paste, but there is no specific disclosure of how to generate ultra-fine grained SiC from a reaction between optionally added  $\text{SiO}_2$  and/or carbon black (or pyrolyzed binder) nor of the specific qualities of such  $\text{SiO}_2$  and/or carbon black necessary for obtaining ultra-fine grained SiC capable to effect sintering of the coarse-particle SiC.

WO 89/09648 (PCT/DK 89/00083), EP patent application No. 0 336 883, EP patent No. 0 336 883 B1, US patent Nos. 5,195,319 and 5,497,620, all belonging to the same patent family, disclose in example 3 the production of porous SiC filter bodies manufactured from SiC grains of a size of 75-170  $\mu\text{m}$ , a "green" or volatile binder and a permanent or ceramic binder. Methylcellulose, clay and carbon black in a total amount of 5-15 percent by weight are used as volatile or "green" binders, whereas 0.2 percent by weight of glycerol and

alcohol are used as viscosity control agents, and water and alcohol are further used as solvents in an amount of 20-25 percent by weight. From the mixed components constituting together a paste, "green" bodies are produced, which "green" bodies are dried and then heated to a temperature of 1500° - 1900°C for generating the permanent or ceramic binder and sintering the bodies together. When the sintering process was carried out in the atmosphere the clay binder generated a glass-mullite bonding, and when carrying out the sintering process in an N<sub>2</sub> atmosphere a silicon nitride bonding was generated from the clay binder. It is further stated: It is believed that micro-crystalline silicon carbide may be used in connection with porous SiC filter bodies. The use of such micro-crystalline SiC together with the SiC particles having a size of 75-170 µm as a permanent binder in the sintered body is claimed in claim 3 of US 5,497,620.

The above quotations being the most pertinent matter of the above documents, none of these documents contain disclosures anticipating neither the novelty nor the inventive merits of the present inventive methods defined in the appended claims.

Thus, the present invention for the first time provides a practicable method of producing a porous structure comprising a mixture of relatively coarse alpha-SiC primary particles bonded together by gas phase deposited SiC produced *in situ* from a silicon source and a carbon source.

### Summary of the invention

The present invention provides a new manufacturing technology based on primary powders for porous ceramic structures and ceramic bodies suitable for numerous products, primarily within the filtration industry. The invention creates a span of porous material ranging from 0.05 µm to 250 µm in pore size with porosity ranging from 20-50%. The ceramic structure is based on specific selected and narrow sized SiC ceramic grains giving the basic porous structure. This may be a porous structure of a membrane carrier or support if designed as a filter body and is characterised by causing a low pressure drop within fluids,

such as liquids and gases, even in the case with a honeycomb membrane carrier having wall thickness ranging from 0.4 to 5 mm. Or the ceramic structure may be an SiC membrane mounted on top of a membrane carrier or support, said silicon carbide membrane being as thin as 0.05 to 1 mm. In this case the  
5 membrane will act as the filtering structure to build up the filter cake and the membrane carrier will support the membrane only.

The basic principle of the invention is based on sublimation of a source of nano-sized, so to speak, raw materials contained within the formed structure, said  
10 raw materials being nano-fine carbon and micro to nano-fine silicium sources. The two elements react with each other and transform over the sublimation phase to a glue, which condense at the primary grains' contact points and re-crystallise.

15 Sintering of a coarse grained porous structure of a sublimating material such as SiC is preferably effected by utilising the fact that finer grained materials for thermodynamically reasons are less stable than the coarser particles. This is expressed in terms radii of curvature. Due to the smaller radii of curvature, the fine-grain SiC particle fraction evaporates before the larger radii of curvature  
20 SiC particles. In the vicinity of the sublimation temperature the transport of materials is in the direction from the nano-fine grained material toward the coarser grains and preferable towards points of negative curvature as defined by point contact with concave surface nature, the driving force being quantified by the numerical difference in curvature. Thus, the optimal case is based on  
25 nano-sized material sources such as gas phase grown nano-size beta SiC obtained by the reaction of silicon vapour with nano-sized residuals from pyrolyzed binders or a carbon source. In the prior art the sub-micron grain materials have been in the range of 0.5-10  $\mu\text{m}$  alpha-SiC combined with coarse grained particles being 30-100  $\mu\text{m}$  alpha SiC. Hereby the obtainable pore size  
30 has been in the range from 5 to 100  $\mu\text{m}$ . The conventional technology do not allow manufacturing of porous structures having pore sizes less than  $\sim 3 \mu\text{m}$ , i.a.

due to the fact that there is no binder system based on sub-nano-size SiC powder to bind the particles in size 5-15  $\mu\text{m}$  at their contact points.

5 According to the present invention the range of pore sizes obtainable is expanded considerably towards finer pores, like micro-pores and nano-pores. This principle opens the potential of producing not only membrane carriers, but also micro- and nano-porous membranes from SiC.

10 The porous filter body may have pore sizes so large that the filter body alone is unable to obtain the desired filtering efficiency. In this case, a membrane having pore sizes smaller than that of the filter body can be added to the filter body to increase the filtering efficiency. As such membrane may be manufactured quite thin, the overall pressure drop over the filter body will not be dramatically increased, however, the filtering efficiency of the filter body may be  
15 exceptionally increased.

Alternatively the present invention may also be used for the production of dense bodies having from 1 - 10% porosity suitable for applications such as resistance heating elements, heat exchangers, catalyst carriers, or the like.

20 The forming method may be by extrusion, casting, stamping or pressing. For extrusion a paste based on primary silicon carbide particles having a high viscosity obtained by the addition of an organic binder is preferred, which during drying will form a low temperature solid non-porous body that in a furnace under  
25 protective atmosphere converts under pyrolyzing conditions to a medium temperature carbon binder. An added silicon source will then melt and react with the organic particles at higher temperatures which creates nano-fine beta SiC which subsequently converts to nano-fine alpha SiC which at very high temperatures sublimates to a gas followed by gas condensing at the primary  
30 particles' grain boundaries, bonding the primary particles together to form a rigid porous body.

Thus, the present invention is based on the creation of nano-fine beta-SiC particles within the body structure itself during the firing process and the omission of separate micro-crystalline or ultra-fine grained silicon carbide to the extrusion recipe, such as those of the FCP group from Norton in Norway. The composition ready for extrusion within the temperature range of 10-80°C must contain a silicon source such as ultra-fine silicon metal powder, silica, or quartz having grain sizes ranging from 0.01-10 µm. Alternatively silicon containing fluids like silicones or silanes can be used as the nano-size silicon source.

Carbon black or carbon powder added to the composition containing an organic binder which during firing at 300-600°C temperature in a non-oxidising atmosphere will also act as a carbon source. During further sintering the silicon source will melt and react with some of the excess carbon and convert to nano-fine beta SiC in the interval of 1250-1600°C and further on to nano-fine alpha SiC in the range of 1600-2300°C. Then it sublimates to a pure SiC gas at temperatures between 1900-2300°C and condenses to solid matter directly at the grain boundaries of the large primary grains.

The present invention is remarkable in that no micro-crystalline silicon carbide powder is included in the extrusion composition and is thus clearly distinct from such briefly mentioned in US patent 5,195,319, example 3 of which mentions most oxide based binder systems, which anyone skilled in the art will know will not give the properties described herein. Furthermore anyone skilled in the art will know that SiC particles do not bond at all in a sintering process. Only by comprising a binder system SiC grains may bond together. Therefore, it is assumed that the binder system is based on micro-crystalline silicon carbide as mentioned in said example 3. Furthermore, the micro-crystalline is stated as the permanent binder in US patent 5,497,620, claim 3, which is a continuation of US patent 5,195,319.

The present invention relies purely on the creation of a nano-size beta SiC sublimation binder system within the structure and on the use of primary silicon

carbide in coarse sized grains from the FEPA selection, which is the international classification of particles.

5 It is advantageous that the remarkable grain boundary growth takes place during the high temperature firing. Only hereby the distance between the coarse grain is kept constant. The firing shrinkage has been measured to be app. 2% linear, which is considered being very low. Hence, the body shape, dimensions, porosity and pore size are kept constant. Furthermore, the process creates no micro-crystalline silicon carbide particles agglomeration in between or around  
10 the grain boundaries or secondary metallic or ceramic phases in between the large SiC grains. Such excess particles will have a negative influence by adding to the pressure drop over the porous body. The structures appear after the firing process as a 100% re-crystallised body wherein the only appearing large grains interconnect perfectly to each other.

15

It may be preferred to manufacture a porous filter body having pore sizes so large that the filter body alone is unable to provide the desired filtering efficiency. In this case, a membrane having pore sizes smaller than that of the filter body may be added to the filter body to increase the filtering efficiency. As  
20 this membrane may be manufactured quite thin, the overall pressure drop over the filter body will not be dramatically increased, however, the filtering efficiency of the filter body may be exceptionally increased.

The membrane coating may be very thin, from e.g. 0.02-5 mm, preferably  
25 0.05-0.4 mm thick. The base structure will have a mean pore size in the range of 10-300  $\mu\text{m}$ , preferably 5-50  $\mu\text{m}$  and the membrane will have a preferred mean pore size in the range of 0.1-5  $\mu\text{m}$ , more preferably 0.2-1  $\mu\text{m}$ .

A membrane may be manufactured in numerous ways. The overall purpose of  
30 the membrane is to decrease the pore size of the filter body in part thereof. As described above, the membrane is preferably added to the filter body as a thin layer. Thus, the membrane should reduce the pore size in a thin layer of the

porous structure of the filter body at its filtering surface. This effect may be obtained either by fastening a separate layer having a suitable pore size to the surface of the filter body or by actually reducing the pores in this part of the filter body.

5

Membranes may be added to the filter body in a number of ways. Such as adding the membrane to a filter body by preparing a slurry containing particles or fibres and to pass under pressure of 0.1-1 Bar the slurry through the filter body porous structure to produce the membrane. Such method, in which the support filters the membrane from the slurry, may be called pressure casting. When the size of the particles or fibres is chosen correctly depending on the pore size of the filter body, these particles or fibres will be filtered off by the filter body when flowing the slurry through the filter body. If the particles or fibres of the slurry are smaller, such as 1-20  $\mu\text{m}$  smaller than the mean pore size of the filter body, these particles or fibres will be filtered off in the outermost layers of the filter body and thus reduce the pore size of this thin layer of the filter body.

10  
15

Membranes may also be added to the membrane support by the drainage casting method. The membrane is prepared as slurry containing the various liquids and particles to pass vertically through the many honeycomb structure channels. Usually at atmospheric pressure, but could be performed under pressure of 0.1-1 Bar. The porous support structure will due to the capillary forces from the pores attract the liquid and adsorb particles from the slurry onto the filter body porous structure to produce the membrane layer.

20  
25

Powder based membranes are preferably multi-layered coatings having increasing grain size from the outside towards the base structure.

Fibre based membranes of fibres having diameters of between 1 and 20  $\mu\text{m}$  have been manufactured. The fibre diameter is preferably between 2-4  $\mu\text{m}$ , and the fibre length is typically in the range of 10-10000  $\mu\text{m}$ , preferably 50-1000  $\mu\text{m}$ , more preferably 100-500  $\mu\text{m}$ .

30

Membranes can be manufactured from oxide ceramic powder or oxide ceramic fibres or from a combination of both, which is the most common used ceramics for membranes.

5

A non-oxide membrane technology has not been found in the patent literature. The broadness of the present invention opens up for applying a silicon carbide membrane to a silicon carbide membrane carrier.

10 It is also the object of the invention to provide a porous structure for an improved cross flow filtration device based on the extreme span in practical use of the invention. Such filtration device may preferably be based on a porous membrane carrier having pore sizes in the range of 1-25  $\mu\text{m}$  and a porous membrane having pore sizes in the range of 0.05-5  $\mu\text{m}$ , both the carrier and the  
15 membrane being manufactured from silicon carbide, but with a relative large difference in pore size suitable for the specific application. A device according to the invention can be described as a cross flow filtration device, from which filtrate and retentate are extracted. However, it is to be recognised that the invention also relates to a porous monolith used as a support for a specific  
20 membrane from which permeate and retentate are extracted.

Hereinafter, the term "cross-flow filtration device" encompasses a porous monolith support for a membrane device and the term "filtrate" encompasses permeate extracted from a membrane device. Such membranes can include  
25 separation barriers suitable for cross flow micro-filtration, ultra-filtration, nano-filtration, reverse osmosis, gas separations, and pervaporation.

The above description describes a cross-flow filtration device, it is to be recognised that this term describes a device, which has a structure that allows  
30 introduction of a feed stock and withdrawal of retentate and filtrate. However, it is to be understood that this structure can be operated in either a cross-flow



mode or in a dead-end mode in which nil or a very small retentate flow is withdrawn.

### Brief description of the drawings

- 5 Fig. 1 is an illustration of a green stage and dried body containing primary  $\alpha$ -SiC particles, an organic binder, silicon metal or silica particles, and extra carbon particles physically dispersed evenly in between the primary  $\alpha$ -SiC particles and throughout the binder mass like a solid 3D network.
- 10 Fig. 2 is an illustration of a heated body after a pyrolyzing process at 300-450 °C, containing primary  $\alpha$ -SiC particles, silicon metal or silica particles and carbon particles physically dispersed evenly in structure. Furthermore, a micro porous carbon skeleton in between the primary silicon carbide particles binds the particles together in an open and porous 3D network created by the carbon
- 15 pyrolyzed from the organic binders.

Fig. 3 is an illustration of a filter structure heated to about 1250-1600°C, containing primary  $\alpha$ -SiC particles, created nano-fine beta SiC particles, but no free silicon metal particles and limited associated carbon particles are present.

- 20 Reaction:  $\text{Si (melt)} + \text{C (solid)} \rightarrow \beta\text{-SiC (nano)}$

Fig. 4 is an illustration of a porous structure after firing at 1900-2300°C containing  $\alpha$ -SiC particles, but no micro-crystalline particles of any kind. Visible through an SEM photo are the re-crystallised primary SiC grains only.

- 25 Performed reaction:  $\beta\text{-SiC (solid nano)} \rightarrow \text{SiC (gas)} \rightarrow \alpha\text{-SiC (solid nano)}$ .

### Example 1

A series of silicon carbide powder technology bodies were manufactured using an extrusion process. The plastic pastes for extrusion were mixed as set forth in

- 30 Table 1-1 below from combinations of the following constituents:

- inexpensive, commercially available F-220 SIKA 1 grinding grains
- commercially available ultra-fine silicon metal powder

- commercially available sub-micron SiC powder type FCP-15 from Norton
  - ultra fine carbon powder such as graphite and carbon black
  - methylhydroxyethylcellulose from Hoechst type MH300
  - water
  - 5 - ethanol
  - stearic acid
  - 1,2-ethandiol
  - polyvinylalcohol PVA Mowiol
- 10 After mixing of the ingredients the pastes produced were extruded in an auger extruder provided with a vacuum chamber into a 25 mm diameter honeycomb die head with 90 cells per square inch. Extrusion speed was app. 1 metre/min.

- After a high temperature sintering process at temperatures above 2300°C in a
- 15 protective atmosphere, such as Argon or Nitrogen, for about 2 hours, the body became a low density, rigid and highly porous structure.

- Sample R was manufactured in accordance with *example 1 in WO 00/01463*. Samples A, B and C illustrates the principle of replacing the "ultra-fine" grained
- 20 SiC (also designated sub-micron or micro-crystalline SiC type FCP-15 having grain sizes ranging from 0.6-10 µm) partly or fully with silicon metal or combinations of silicon metal and carbon (Table 1-1). In all cases the resulting bodies were rigid and strong porous structures of identical properties.

25 Table 1-1 Composition of compounds

Material wt%	R	A	B	C
F-220	1875	1875	1875	1875
FCP-15	<b>375</b>	<b>0</b>	<b>0</b>	<b>188</b>
Silicon metal	<b>0</b>	<b>263</b>	<b>263</b>	<b>66</b>
C – Carbon	<b>0</b>	<b>113</b>	<b>0</b>	<b>28</b>
MH 300	144	144	144	144
PVA-solution	37,5	37,5	37,5	37,5

Stearic acid	37,5	37,5	37,5	37,5
1,2 ethandiol	12,5	12	12	12
Water	138	138	138	138
Ethanol	325	325	325	325

The resulting porous structures were oxidised at 900 °C for 2 hours in order to remove residual carbon and water flux was determined at 0.4 and 0.2 bar pressure differences. The test results are given in Table 1-2. It is seen that the performance of both the fully and partly substituted compositions A, B and C are equal to or better than the R-sample prepared according to the prior art technique.

Table 1-2 Composition ratio, oxidation weight losses and water flux.

Sample	FCP: F-220	Si: F-220	C: F-220	Weight loss %	Flux <sub>0,4bar</sub> M <sup>3</sup> /m <sup>2</sup> h	Flux <sub>0,2bar</sub> M <sup>3</sup> /m <sup>2</sup> h	Porosity %
R	0,2	0,00	0,000	-0,76	25,4	15,8	44,2
A	0,1	0,07	0,032	-0,99	25,4	15,8	44,3
B	0,0	0,14	0,000	+0,22	25,9	16,3	45,8
C	0,0	0,14	0,060	-1,35	-	-	44,3

### Example 2

A series of Silicon Carbide powder technology bodies were manufactured using an extrusion process. The plastic pastes for extrusion were mixed from combinations of the following constituents:

- inexpensive, commercially available F-220 SIKA 1 grinding grains
- commercially available ultra-fine silicon metal powder
- inexpensive, commercially available fine grained SiO<sub>2</sub> powder
- ultra fine carbon powder such as graphite and carbon black
- methylhydroxyethylcellulose from Hoechst such as type MH300
- water
- ethanol
- stearic acid

- 1,2-ethandiol
- polyvinylalcohol PVA Mowiol

After mixing of the ingredients the pastes produced were extruded in an auger extruder provided with a vacuum chamber into a 25 mm diameter honeycomb die head with 90 cells per square inch. Extrusion speed was 1 metre/min.

After a high temperature sintering process at temperature above 1900°C, in a protective atmosphere, such as Argon or Nitrogen, for about 1 hour, the body became a low density, rigid and highly porous structure.

Samples D and G illustrate the principle of replacing the fine grained SiC (FCP-15, see example 1, sample R) fully and in excess with silica (Table 2-1). Samples E and F illustrate the development of sample B in Example 1 replacing the fine-grained SiC (FCP-15, see example 1, sample R) fully and in excess with silicon metal (Table 2-1). In all cases the result were ridged and strong porous structures. The fired resulting structures were oxidised at 900 °C for 2 hours in order to remove residual carbon and the water flux was determined at 0.4 bar pressure difference. The results are given in Table 2-2.

Table 2-1 Composition of compounds

Material wt%	D	E	F	G
F-220	1875	1875	1875	1875
SiO <sub>2</sub>	<b>562</b>	<b>0</b>	<b>0</b>	<b>843</b>
Silicon metal	<b>0</b>	<b>263</b>	<b>526</b>	<b>0</b>
C – Carbon	<b>33,6</b>	<b>34</b>	<b>147</b>	<b>90</b>
MH 300	144	144	144	144
PVA-solution	37,5	37,5	37,5	37,5
Stearic acid	37,5	37,5	37,5	37,5
1,2 ethandiol	12,5	12	12	12
Water	138	138	138	138
Ethanol	325	325	325	325

Table 2-2 Composition ratios and water flux

Sample	SiO <sub>2</sub> : F-220	Si: F-220	C: F-220	Flux <sub>0,4bar</sub> M <sup>3</sup> /m <sup>2</sup> h
D	0,30	0,00	0,018	24.7
E	0,00	0,14	0,018	25.3
F	0,00	0,28	0,078	25.1
G	0,45	0,00	0,048	24.9

### 5 Example 3

The residual carbon obtained from the organic binder after pyrolyzing the green stage and dried body at 300-600°C may be insufficient for the optimum growth of beta silicon carbide based on the silicon available in the structure. Therefore, additional carbon from heavy crude oil distillates, bitumen, asphalt, aliphatic hydrocarbons or the like may be included as a carbon source or binder phase in a water emulsifying emulsion.

### Example 4

A series of inorganic silicon carbide membranes were manufactured using a slip casting process. The slurry were mixed from combinations of the following constituents:

- inexpensive, commercially available F2000 SIKA 1 at 7.6 µm grain size
- commercially available ultra-fine silicon metal powder
- inexpensive, commercially available fine grained SiO<sub>2</sub> powder
- ultra fine carbon powder and/or carbon black
- methylhydroxyethylcellulose from Hoechst MH300
- water
- Darvan C
- polyvinylalcohol PVA Mowiol

The slurry was added as a thin layer to an extruded body wall surface by flowing the slurry through the passageways of the body. The slurry added to the support walls was dried at room temperature. After a high temperature sintering process at temperatures above 1700°C, in a protective atmosphere, such as Argon or Nitrogen, for about 1 hours, the structure became a highly porous membrane. The thin layer was in the range of 0.05 to 0.5 mm thick and had pore sizes in the range of 0.5-1  $\mu\text{m}$ .

While the present invention has been described in connection with particular embodiments thereof, it will be understood by those skilled in the art that many changes and modifications may be made without departing from the scope of the invention as defined by the appending claims.

## Claims

1. A method for preparing a ceramic porous structure comprising a mix of:

- alpha silicon carbide primary particles having a size ranging between 1 and 475  $\mu\text{m}$

- 5 - a silicon source other than an SiC compound
- organic particles having a size of 0.00001-20  $\mu\text{m}$
- at least one organic binder

forming a paste or fluid from said mix and selected suitable liquid(s), forming the paste into a green body and drying it at low temperatures to form a solid non-porous body, subjecting said body to pyrolyzing conditions in a furnace under a protective atmosphere to convert the organic binder to a medium temperature carbon binder, melting the silicon source and reacting it with the carbon binder or particles at high temperature thus creating nano-fine beta-SiC, which is further converted to nano-fine alpha-SiC and at very high temperature sublimated to a gas followed by condensing said gas at the primary particles grain boundaries so as to bond the primary particles together to form a rigid porous structure.

2. A method for preparing a ceramic porous structure according to claim 1, wherein said silicon source is a silicon metal having a particle size of 0.01-30  $\mu\text{m}$ .

3. A method for preparing a ceramic porous structure according to claim 1, wherein said silicon source is silica having a particle size of 0.001-20  $\mu\text{m}$ .

4. A method for preparing a ceramic porous structure according to claim 1, wherein said silicon source is a silicone or silane in liquid stage.

5. A method according to any of the previous claims, wherein the compound for preparing the porous structure combines heavy crude oil distillates, bitumen, asphalt, alifatic carbon or the like as the carbon source or binder phase in a water emulsifying emulsion.

6. A method according to any of the previous claims, wherein the compound for preparing the porous structure combines both Silica powders and Silicon metal powders in combination with organic material in order to form nano-fine Beta silicon carbide within the structure during the firing process.
7. A silicon carbide structure prepared according to any one of the claims 1-6, wherein the ceramic body or support has porous walls defining a honeycomb monolith comprising a matrix of parallel wall/cells extending axially through the body.
8. A silicon carbide structure prepared according to any one of the claims 1-6, wherein the body has porous walls defining a structure with separately arranged parallel extending channels.
9. A silicon carbide structure prepared according to any one of the claims 1-6, wherein the body is a foam structure or a combination of claim 7 or 8 and a foam structure.
10. A silicon carbide structure prepared according to any one of the claims 1-6, wherein the pores are formed by adding a pore forming organic agent.
11. A porous silicon carbide membrane structure for filtration purposes prepared according to any of one the claims 1-6, for separating particles or the like in pressurised fluids or gases by means of porous structures of particulate Silicon Carbide material having a porosity of 10-50% and a selected pore size ranging within 0.005 to 55  $\mu\text{m}$ .
12. A porous Silicon Carbide membrane coating suitable for micro- / ultra- / nano- filtration, or reverse osmosis, or gas separations, or pervaporation purposes according to claim 11, bonded to the surface of a porous silicon carbide membrane carrier by means of a casting process.



13. A porous Silicon Carbide multi-layer membrane coating suitable for micro- / ultra- / nano- filtration, or reverse osmosis, or gas separations, or pervaporation purposes according to claim 11, bonding the layer to the respective layer and to the surface of a porous silicon carbide membrane carrier hereby obtaining a reduction in pore size with increasing number of layers.

14. A method according to any one of the claims 1-6, wherein the particles on which the material of the porous structure is based comprises SiC particles sized in the interval 1-475  $\mu\text{m}$ , and wherein the sintering of the shaped body takes place at a temperature in the interval 2200-2600°C in protective atmosphere.

15. A method according to any one of the claims 1-6 and 14, wherein the shaping of the porous body is performed by extrusion.

16. A method according to any one of the claims 1-6, 14 and 15, wherein the shaping of the porous body is performed by casting or as uniaxial compression process or as isostatic compression process.

17. A filter device prepared according to any one of the claims 1-6 and 14-16, for separating particles from a particle containing fluid.

18. A device prepared according to any one of the previous claims 1-6 and 14-16, wherein the body is a honeycomb structure.

19. A filter device according to claim 17, wherein the body is a honeycomb structure with cross-flow filtration characteristics and appearance.

20. A filter device according to claim 17, wherein the body is a cross-flow filtration device with integrated conduit network for carrying filtrate towards the

filtration collection zone, the filtrate conduit network providing paths of lower flow resistance than that of the membrane carrying walls.

21. A filter device according to claim 17, wherein the body is a dead-end filtration unit characterised by a multi-plum of parallel passageways extending from one end of the device to the opposite end, every second passageway closed in one end corresponding the neighbour channel being open in the opposite end, hereby forcing the fluid to pass only the porous body wall perpendicular.

22. A filter device according to any of the claims 17-21, wherein filter passageways is covered with a fine pored selective membrane.

23. A method of separating a feed stream in a cross-flow filtration device into a filtrate and a retentate, which method comprises:

- a) providing a cross-flow filtration device according to claim 17;
- b) introducing a feed stream into the feed end face of the structure and into a plurality of the passageways for separation into a filtrate and retentate;
- c) flowing the filtrate from the passageways through the intersegment filtrate conduit;
- d) collecting the filtrate from the intersegment filtrate conduit zones in the external collection zones, and
- e) removing the retentate from the retentate end face of the structure

24. A filter device for separating particles from a particle containing flue gas.

25. A filter device according to claim 24, wherein the body is a honeycomb monolith or a honeycomb-like structure.

26. A filter device according to claim 24, wherein the body is a dead-end filtration unit characterised by a multi-plum of parallel passageways extending

from one end of the device to the opposite end, every second passageway closed in one end corresponding the neighbour channel being open in the opposite end, hereby forcing the gas to pass only the porous body wall perpendicular generating a wall-flow-filter.

5

27. A filter device or filter assembly according to any of the preceding claims, wherein at least one side of the filter body wall is covered with a wash coat and or a catalytically active coating.

10

28. A filter device or filter assembly according to any of the preceding claims, wherein the filter body wall matrix itself is covered with a wash coat and or a catalytically active coating.

15

29. A filter device or filter assembly according to any of the preceding claims, wherein at least one side of the filter body wall is covered with a surface increasing coating and a catalytically active coating.

20

30. A filter device or filter assembly according to any of the preceding claims, based on a body made from course grained Silicon Carbide particles ranging between 25 and 475  $\mu\text{m}$

25

31. A filter device or filter assembly according to any of the preceding claims, used in combination with a diesel engine or in conjunction with a diesel engine in a transportation vessel, in a vehicle or on a stationary diesel engine, a gas turbine in a power-generating plant.

30

32. A filter device or filter assembly according to any of the preceding claims, used in combination with a combustion source, wherein the fluid is a flue gas from a coal burning or coal gasification apparatus wherein the fluid is a hot flue gas from a PFCB, Pressurised Fluid Combustion Bed plant or a incineration plant

33. A method according to claim 23, wherein the filter unit, apparatus is characterised by the means for removing solid particles accumulated on the said filter surface comprising a means for supplying a back flushing fluid or gas.

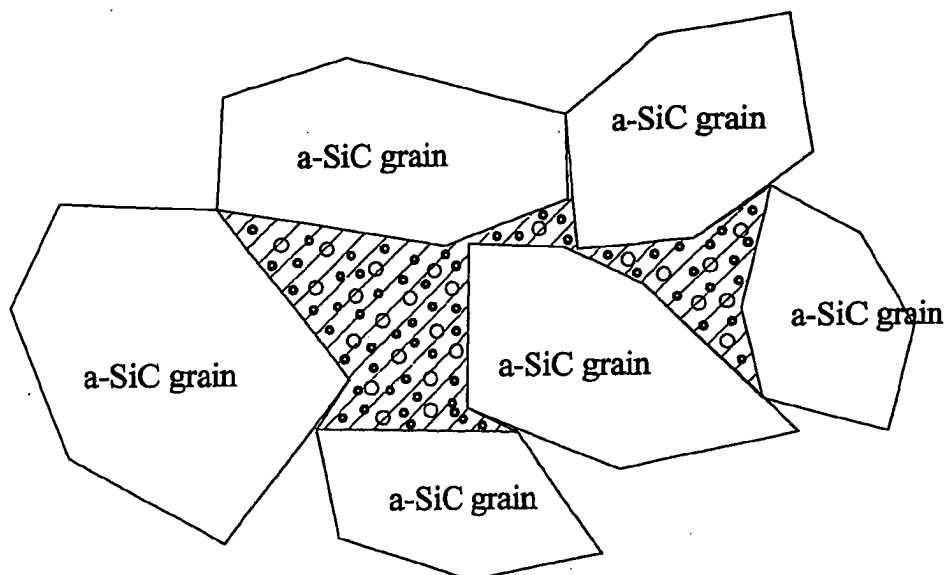
5 An apparatus for filtering particles from a gas or liquid, the apparatus containing a filter body, wherein, the filter body has a gas or liquid inlet side surface and an opposite gas or liquid outlet side surface, a first plurality of blind filtration cavities extending perpendicularly into said body from said inlet side surface and a second plurality of blind filtration cavities extending perpendicularly into  
10 said body from said outlet side surface, said blind filtration cavities of said first and second pluralities being arranged spaced apart and mutually juxtaposed, and wherein the filter body is composed of a number of longitudinal porous filter elements assembled so as to form said filtration cavities.

34. A method for filtering particles from a gas or liquid using a filter body having  
15 a gas or liquid inlet side surface and an opposite gas or liquid outlet side surface, a first plurality of blind filtration cavities extending pendicular into said body from said inlet side surface and a second plurality of blind filtration cavities extending perpendicularly into said body from said outlet side surface, said blind filtration cavities of said first and second pluralities being arranged spaced apart  
20 and mutually juxtaposed, the filter body being composed of a number of longitudinal porous filter elements assembled so as to form said filtration cavities, the method comprising transmitting the gas or liquid into the first plurality of blind filtration cavities and through the porous filter elements into the second plurality of blind filtration cavities.

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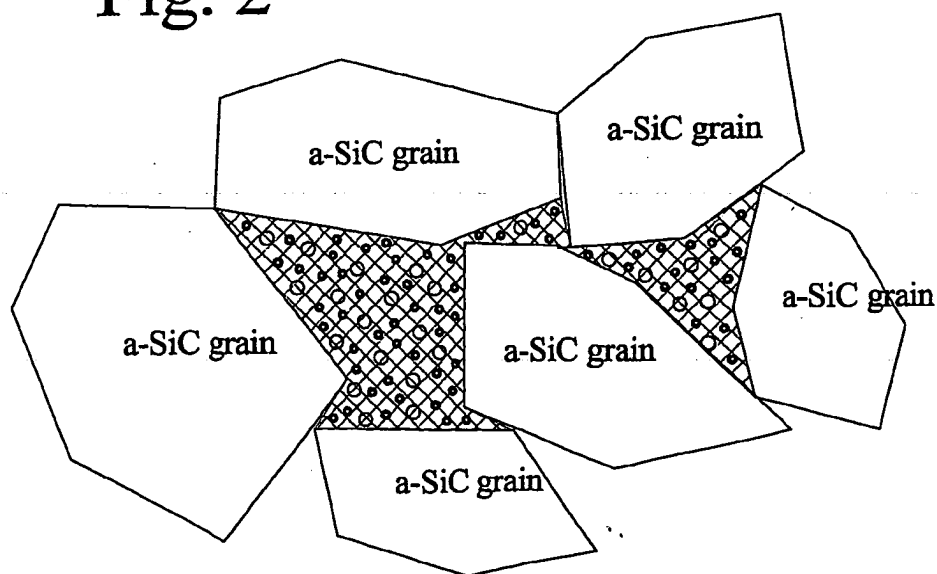
Fig. 1



Green body grain structure  
 Manufacturing temperature range 10-80°C  
 Alpha SiC (a-SiC grains)

- - Carbon black or graphite
- - Si or SiO<sub>2</sub>
- ⊗ - Organic binders

Fig. 2

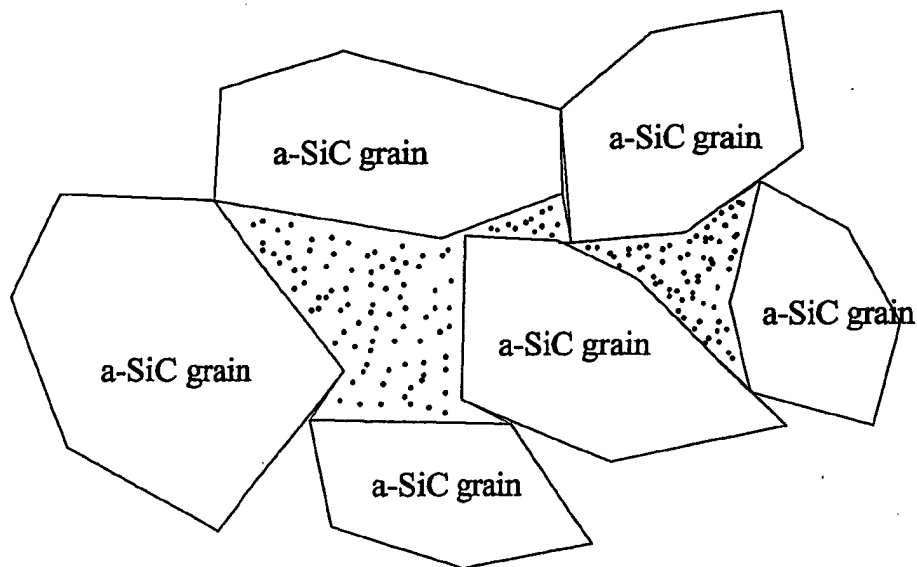


Pyrolysed grain structure  
 Pyrolysing temperature range 300-450°C  
 Alpha SiC grains (a-SiC Grains)

- - Carbon black or graphite
- - Si or SiO<sub>2</sub>
- ⊗ - Carbon Skeleton

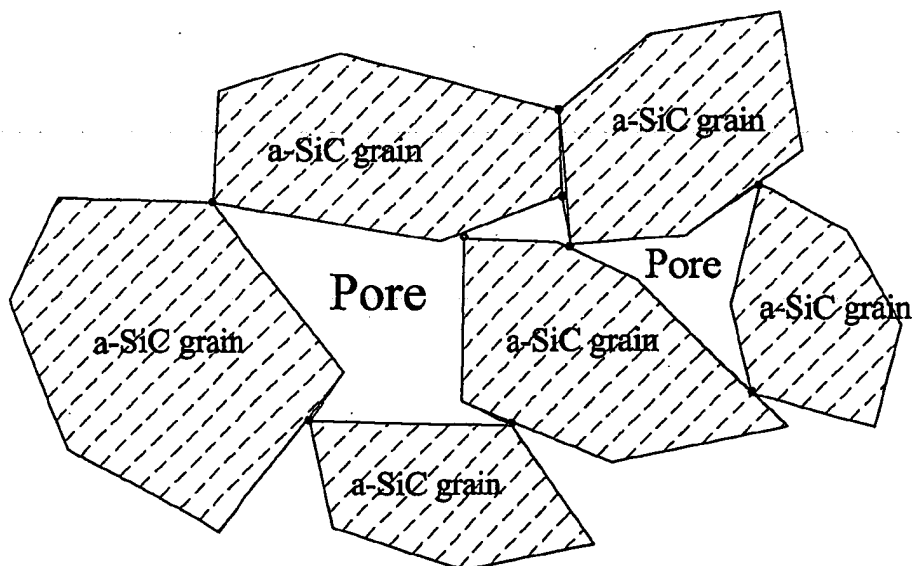
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Fig. 3



Intermediate grain structure  
 Heating temperature range 1250-1600°C  
 Alpha SiC grains (a-SiC Grains)  
 • - Sub-Nano Beta particles

Fig. 4



Re-crystallized SiC grain structure  
 Re-crystallization temperature 1900-2300°C  
 Pure Re-crystallized Alpha grains (a-SiC grain)  
 Sub-Nano Beta converted to Alpha in grain contact points

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 02/00618

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C04B 38/00, F01N 3/02, F01N 3/022, B01D 46/24, B01D 46/10  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C04B, F01N, B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	--	22
X	WO 9422556 A1 (STOBBE, PER), 13 October 1994 (13.10.94), page 1, line 21 - page 2, line 17; page 4, line 22 - line 26; page 6, line 15 - page 11, line 3, page 12, line 20; claims 1-40; abstract	7-11,17-21, 24-32
Y	--	22

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 02/00618

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	--	22
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Information on patent family members

01/12/02

International application No.

PCT/DK 02/00618

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